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Azoporphyrin – the porphyrin analogue of azobenzene [**]

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Azobenzenes (1,2-diaryldiazenes) are very important organic pigments, and they have a unique place in the field of photoresponsive conjugated molecules due to their (usually) reversible *E*/*Z* photoisomerisation.[1] The current intense interest in molecular analogues of mechanical components and information storage and processing elements has stimulated research into conjugated molecules whose shape and/or optical properties can be switched electro- or photochemically.[2] Among the classes of conjugated pigments being explored in these contexts are the porphyrinoids, which offer advantages of intense light absorption, a variety of accessible oxidation states, and synthetic control of properties through peripheral or central substitution.[3] Extension of porphyrinoid conjugation can be achieved by linking the peripheral carbons either by three direct bonds (as in the "porphyrin tapes" of Osuka et al.)[4] or through potentially conjugating bridges such as alkenes[5] or, even better, alkynes.[6]

Anderson and co-workers compared both experimentally and theoretically the strength of porphyrin-*aryl* electronic coupling through alkene, alkyne, imino and azo (diazeno) bridges. They found the last of these to be the most efficient, combining good orbital matching through continuous sp^2 conjugation, with less steric interference than the alkene linker.[7] Thus 1,2-di(porphyrinyl)diazenes ("azoporphyrins", e.g. **1**) are desirable synthetic targets, combining extended porphyrinoid conjugation with potential photoreactivity of the azo linkage.[8] Herein we describe the convenient synthesis and crystallographic and spectroscopic characterisation of the first *E*-azoporphyrins.

<Str 1.cdx>

Azobenzenes can be prepared by a variety of well known reactions,[9] such as partial reduction of nitro-, nitroso- or azoxyarenes, coupling of arylamines with nitrosoarenes, azo coupling of aryldiazonium salts with electron-rich arenes, and one-pot Cu(I) mediated coupling/oxidation of bis(Boc) arylhydrazines and aryl halides.[10] Anderson reported that the azo coupling route was unsuccessful in forming **$Zn_2$1b**.[7] Our initial approach was Pd-catalysed coupling of monoprotected hydrazines (carbazates) with bromoporphyrins, but this generated a variety of products including novel diiminoporphodimethenes.[11] When unsubstituted hydrazine was employed with bromoporphyrin **Ni2a**, we isolated the primary amine **Ni3a** and the Ni(II) complexes of the corresponding bis(porphyrinyl) secondary amine and 5-hydroxyporphyrin, in proportions that varied with the initial stoichiometry.[12]

While trying to improve the yield of the secondary amine from the coupling of **Ni2a** with **Ni3a**, using catalyst/base system $Pd(OAc)_2$/*rac*-BINAP/Cs_2CO_3 in toluene, we found that a very minor golden brown product was always apparent on TLC plates. The visible absorption spectrum of this compound corresponded with that expected for the elusive target **$Ni_2$1a**. This product could arise simply from oxidative dimerisation of primary amine induced by the metal salt, so we omitted **Ni2a** and changed to copper(II) acetate/pyridine, under air as reoxidant. We were pleased to find that this is a very clean method of coupling **Ni3a** to form **$Ni_2$1a** in high yield, with no side products (Scheme 1). Indeed, with longer heating, even 2 mol % Cu was suitable, but for convenient reaction times we have settled on the conditions given in the Supporting Information.

<Scheme 1.cdx>

Copper promoted formation of azoarenes from arylamines has been largely neglected since its investigation in the 1950s.[13] The reaction was extended to the corresponding zinc(II) complexes, which are favoured by many workers due to their emissivity and ease of demetallation. The preparation of the precursor amines **Ni3a** and **Zn3a** from free base triphenylporphyrin **$H_2$4a** has been streamlined to give respective yields of 68 and 58% for the sequence nitration, metallation, and reduction, with purification only after the final step (Supporting Information). Alternatively, **Ni3a** can be obtained by the hydrazine route.[12] **$Zn_2$1a** was demetallated with TFA in toluene, giving the free base azoporphyrin **$H_4$1a.** All three examples are very insoluble in common solvents, although the metal complexes are more soluble in the presence of pyridine.

Single crystals of **$Ni_2$1a·py** were grown by diffusion of methanol into a pyridine solution and the crystal structure was determined by X-ray analysis.[14] The molecule (Figure 1) has crystallographic inversion symmetry with the inversion centre on the N(5)–N(5′) bridge. The pyridine solvent has 2-fold symmetry, with the N atom disordered equally across the six pyridyl atom positions. The asymmetric porphyrin ring is considerably distorted from planarity, as is typical for Ni(II)-bound porphyrins. The maximum deviations of atoms from the mean plane of the $C_{20}N_4Ni$ porphyrin component occur for the meso carbon atoms C(5) and C(15) (0.682 Å and 0.546 Å, respectively) and C(10) and C(20) (0.555 Å and 0.609 Å, respectively). The ring distortion projects C(5) and C(15) on one side of the mean plane of the ring and C(10) and C(20) on the other, in the manner described in the literature as "ruffled".[15] The mean plane of the N_4Ni coordination sphere is almost co-planar with that of the mean plane of the porphyrin ring (dihedral angle 0.55° with a perpendicular distance for Ni···$C_{20}N_4Ni$-plane of 0.010 Å). The mean $C_{20}N_4Ni$ planes of the porphyrin rings are exactly parallel and off-set by a perpendicular distance of 3.189 Å. This displacement is a consequence of the ring distortion (which projects C(5) and therefore the azo-bridging nitrogen N(5) away from the plane of the ring), and the twisted conformation of the azo-bridge. The dihedral angles between the C(5)-N(5)-N(5′)-C(5′) mean plane and the mean porphyrin planes are 37°. This out-of-plane twist of the azo bridge is significantly smaller than those of the alkene bridges in *E*-ethenediyl linked Ni_2 (50°)[5e] and Zn_2 (47°)[5c] dimers.

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<Figure 1.tif >

Extension of porphyrin conjugation and electronic interaction with unsaturated substituents give rise to well known features in the electronic spectra, namely red-shifting of absorption and emission bands, increase in relative intensity of the Q bands versus the B (Soret) bands, and splitting of the Soret band. These features have been intensively studied.[6,7] The visible absorption spectra of azoporphyrins possess all these characteristics, as shown in Figure 2. The Ni(II) complex displays a large complexation shift (Q band 749 to 830 nm) when excess pyridine is present – presumably the Ni(II) centres are then six-coordinate (Figure 2, upper). The extent of "interporphyrin communication" can be assessed qualitatively by means of the energy gap between the two main components of the Soret band. Splittings due to different bridges for similar dinuclear Zn complexes are *E*-ethenediyl 2430 cm^{-1},[5e] ethynediyl 3320 cm^{-1},[5c] and azo 3670 cm^{-1} (**$Zn_2$1a**).[16] The HOMO-LUMO gap (lowest energy Q band position) is another measure of expansion of the porphyrin π system. This comparison for C_2H_2/C_2 and azo linkers is complicated by the effects on the HOMO-LUMO gaps of the electronegativity differences of the carbon and nitrogen groups *as substituents*, as well as by the steric demands of the ethene linker. As there is no simple way to separate these factors, we just state that the azo dimer has significantly more red-shifted Q bands, i.e. **$Zn_2$1a** 841, ethynediyl dimer 713,[5c] and *E*-ethenediyl dimer 661 nm.[5e,16] This strong red-shift is reflected also in the HOMO-LUMO gap of **$Zn_2$1a** measured by cyclic voltammetry, $E_1^{ox} - E_1^{red}$ = 1.34 V,[17] which is markedly smaller than those for the ethynediyl (1.98 V) and *E*-ethenediyl (1.92 V) dimers.[5c,17]

<Figure 2.jpg>

The photoisomerisation of many *E*-azoarenes is normally readily achievable. However, for azo linkers in porphyrin/phthalocyanine-containing constructs, results are variable. In some cases, the photoexcited states are quenched so rapidly that no isomerization can be detected,[8a,d] while in others, the isomerization is successful.[3a,c,8b,c] We irradiated solutions of both **$Zn_2$1a** and **$Ni_2$1a** (Supporting Information), but have not seen evidence for isomerisation to the *Z*-azoporphyrin. Evidently, the extended conjugation promotes deactivation of the photoexcited states.

We have tried to extend this chemistry to prepare longer azo-linked oligoporphyrin arrays, using 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin instead of 5,10,15-triphenylporphyrin, to leave an open meso position for further coupling (Scheme 2). However, treatment of amine **Ni3b** under our coupling conditions gave less than 10% yield of the desired azoporphyrin **$Ni_2$1b**, the major product being the remarkable head-to-tail dimer with one iminoporphodimethene ring, **$Ni_2$5**.[18] A second similar product, the corresponding oxo species, **$Ni_2$6**, was also isolated. Clearly, another strategy will be required to prepare larger arrays, as we have so far been unable to prepare the required 5,15-diaminoporphyrins.

<Scheme 2.cdx>

The properties of the azoporphyrins imply a stronger inter-porphyrin interaction across the azo bridge than across ethene and ethyne linkers. In the solid state, the lone pairs on the bridging nitrogens still make their presence felt, resulting in a 37° out-of-plane rotation of the linker. Nevertheless, the prediction[7] that the azo linker would be an attractive "molecular wire" for connecting porphyrins has been fulfilled. Our recent studies of the coupling of nitrogen nucleophiles with porphyrins,[11,12] and now our preparation of the first azoporphyrins, indicate that further studies in this field will be rewarding. In particular, photophysical and non-linear optical studies of azoporphyrins should be interesting.

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[14] *Crystal data*: **$Ni_2$1a**·py; Formula $C_{81}H_{51}N_{11}Ni_2$, M = 1295.75, monoclinic, $P2/c$, a = 13.0693(3) Å, b = 9.7304(2) Å, c = 24.1344(5) Å, β = 104.2410(10), V = 2974.45(11) $Å^3$, D_c = 1.447 g cm^{-3}, Z = 2, crystal size 0.20 × 0.13 × 0.09 mm, blue prism, temperature 150(2) K, λ(Mo-Kα) = 0.71073, μ(Mo-Kα) 0.0.694 mm^{-1}, T(Empirical)$_{min,max}$ = 0.885, 0.944, $2\theta_{max}$ = 59.96, *hkl* range –18 to 18, –13 to 13, –33 to 33, N = 44909, N_{ind} = 8570 (R_{merge} = 0.0266), N_{obs} = 6976 ($I > 2\sigma(I)$), N_{var} = 424, residuals $R1(F, 2\sigma)$ = 0.0423, $wR2(F^2$, all) = 0.0.0958, GoF(all) = 1.023, $\Delta\rho_{min,max}$

= –0.434, 0.450 e Å^{-3}. CCDC-627200 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[17] Measured by cyclic voltammetry in CH_2Cl_2/0.1 M Bu_4NPF_6, Pt working and counter electrodes, Ag/AgCl solid reference electrode, ferrocene at +0.55 V; E_1^{ox} +0.63 V, E_2^{ox} +0.77 V, E_1^{red} –0.71 V, E_2^{red} –0.81 V.

[18] This compound was isolated in 26% yield from reaction of **Ni3b** with 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) and *tert*-butyl nitrite/BF_3.Et_2O in THF at RT. M. J. Smith, DPhil thesis, University of Oxford (UK), **2004** and H. L. Anderson, private communication.